Development of air cleaning materials for formaldehyde in indoor air and evaluation of their removal performance

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1. Introduction

Manganese dioxide(MnO_2) is currently used for a major ingredient of air cleaning materials [1], because it reacts with formaldehyde(HCHO) gas to give carbon dioxide (CO_2) even at room temperature [2]. However, the removal efficiency tends to decrease when used for a long-term under the atmosphere including several hundreds ppm of HCHO. This is probably due to accumulation of intermediates on the surface caused by changes in oxidation state of manganese (reduction from IV to III/II by the reaction with HCHO).

Tang et al. [3] successfully realized a stable complete oxidation of HCHO using manganese-cerium complex oxides (MnO_x-CeO_2) prepared by sol-gel and co-precipitation methods. The effect was explained by a process of oxygen activation and oxygen transfer through redox cycles of manganese and cerium oxides in the composite; the reduced manganese oxide is re-oxidized into MnO_2 by an oxygen reservoir ceria (CeO_2), and the reduced cerium oxide is thus regenerated to CeO_2 by oxygen in air. If the proposed mechanism is true, simply blended powders of each metal oxide should also show the stable oxidation of HCHO, working as like a redox catalyst(Fig.1).

This study aimed to develop a novel composition of MnO_2 based catalyst with longer life-time in oxidative decomposition of HCHO at room temperature. To test the above hypothesis, authors have demonstrated a breakthrough test for 500 ppm of HCHO gas stream employing MnO_2 powders simply blended with CeO_2 powders.
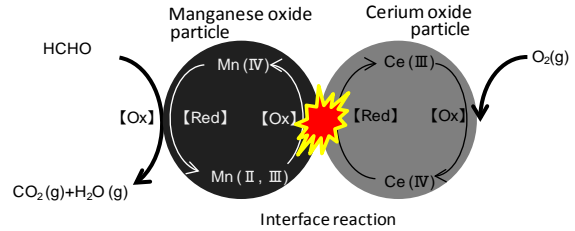

Fig.1 Redox cycle between manganese oxide particle and cerium oxide particle.

2. Experimental

2.1 Sample preparation: The test samples were simply prepared by mechanical mixing of the MnO_2 and CeO_2 powders for 5 min in a test tube with manual shaking.

MnO_2 powder: Activated Manganese Dioxide (AMD, BET surface area: 175 m^2/g, purity: 83.5% and particle diameter: < 5μm), Rreagent grade MnO_2 (RMD, 45m^2/g, > 99%).

CeO_2 powder: Regent grade ceria (RCD, 3.7 m^2/g, purity: 99.99%), fresh ceria-based chemical mechanical polishers (fCMP, 3.0 m^2/g, purity: 68.9%), used CMP (uCMP, 102 m^2/g, purity: 44.7%) and a calcination product from cerium carbonate (CCD, 116 m^2/g, purity: 94%)

2.2 HCHO removal tests: Removal performance of the blended samples for HCHO was evaluated by a breakthrough test. Integrated amounts of HCHO removed during the tests, S_{HCHO}(mmol) were obtained from equation (1) and compared quantitatively among samples.

$$S_{HCHO} = F \int_{0}^{t_b} (C_{in} - C_{out})\mathrm{dt} \qquad (1)$$

where F (m^3/min) is flow rate, t_b(min) is test time, C_{in}(mmol/m^3) is inlet HCHO concentration and C_{out}(mmol/m^3) is outlet HCHO concentration.

3. Result and Discussion

Fig. 2 shows typical time evolutions of inlet and outlet HCHO concentrations obtained from the breakthrough tests of samples RMD+RCD and AMD+RCD, comparing with those of RMD and AMD only.
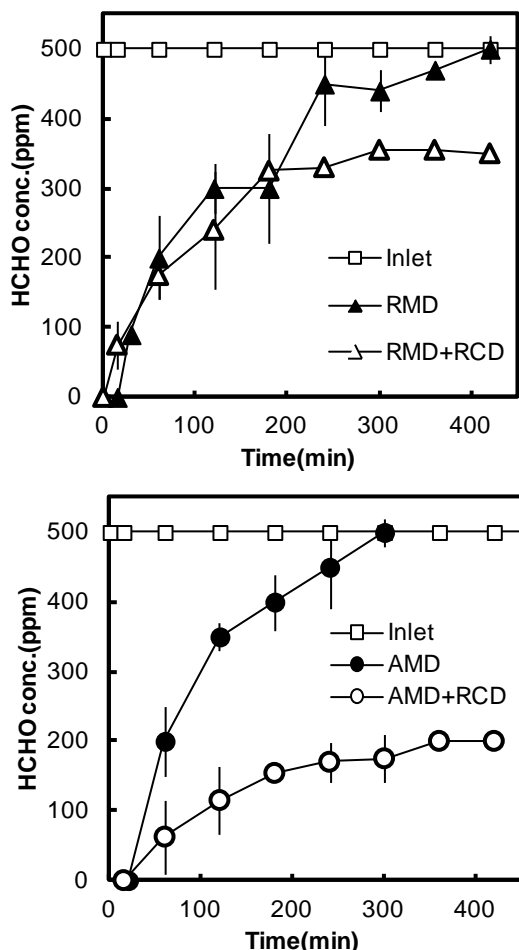

Fig.2 Time evolution of HCHO concentrations obtained from breakthrough tests (*n=2*).

Under this severe condition with a heavy HCHO load, the breakthrough easily occurred within 7 hours (420 min) when using RMD or AMD only. Meanwhile, the effect of blending ceria was remarkable for both samples RMD+RCD and AMD+RCD, resulting in the appearance of steady state removal performance with constant outlet concentrations.

The blending effect was much remarkable for AMD+RCD rather than sample RMD+RCD,

probably because the higher BET surface area of AMD was favorable to the acceptance of oxygen from ceria in order to regenerate the reduced manganese to MnO_2 in the powder mixture.

On the other hand, another ceria powders also improved the removal performance of AMD. Considering S_{HCHO} as RCD=1.27 mmol, fCMP=1.11 and uCMP=0.74, the blending effect appeared in the order of RCD > fCMP > uCMP, following the order of purity. This means the purity of ceria is a significant factor for realizing the blending effect.

The XRD pattern of RCD, fCMP and uCMP were shown in Fig.3. These ceria powders has same XRD pattern, which clearly showed the presence of cubic fluorite structure of cerium dioxide[4]. This suggests the
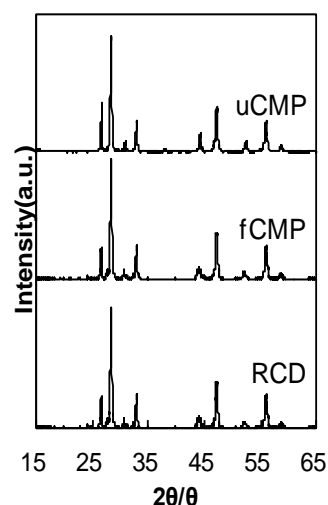

Fig.3 XRD patterns of RCD, fCMP, uCMP served for samples.

cubic fluorite structure of CeO_2 is also essential for demonstrating the blending effect.

4. Conclusions

The HCHO removal performance of MnO_2 was improved by simply blending ceria powders. This finding supports the proposed mechanism that the functional interface between MnO_2 and CeO_2 powders works for the regeneration of reduced manganese oxides by a process of oxygen activation and oxygen transfer through redox cycles.

5. Reference

[1]Y. Sekine et al., *Atmos. Environ.* 35 2001-2007 (2001).

[2]Y. Sekine, *Atmos. Environ.* 36 5543-5547 (2002)

[3]X. Tang et al., *Appl. Catal. B Environ.* 81 115-121(2008)